

OXYGEN-SCAVENGING ARTICLES DEVOID OF VISUAL SPOTS UPON OXIDATION AND RELATED METHODS

CROSS REFERENCE TO RELATED APPLICATIONS

5 This application claims the benefit of United States Provisional
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BACKGROUND OF THE INVENTION

10 This invention relates to the production of a transparent article and,
more particularly, to the production of a shaped, transparent article, such as a
plastic container, bottle, tray or film wrap, including a thermoplastic polymer
matrix having an inorganic oxidizable composition, namely, an oxygen scavenger,
dispersed therein.

15 Thermoplastic resins, such as polyesters and other similar high strength
polymers, are commonly used to manufacture packaging materials. Polyesters,
such as polyethylene terephthalate (PET) and its copolymers, when processed
under the right conditions and optionally stretched to a desired size and shape,
produce high strength articles with excellent gas barrier properties suitable for
practical use in the food and beverage industry.

20 However, certain foods, beverages, and medicines can deteriorate or
spoil if exposed to oxygen. To that end, PET articles have sometimes not been
suitable for some foods, beverages or medicines where extremely low oxygen
permeability is required over a significant period of time on the order of a few
months or more. To improve the shelf life and/or flavor retention of products
25 wrapped or contained in these PET articles, attempts heretofore have been made to
improve the gas barrier protection of the PET articles. For instance, PET is often
supplemented with additional layers of packaging material to prevent oxygen
permeability.

30 Adding a layer of gas barrier film is known as passive-barrier packaging.
Ethylvinyl alcohol (EVOH), polyvinylidene dichloride (PVDC), and polyamides like

poly(*m*-xylylene adipamide) (MXD6), are examples of polymers commonly used for this purpose due to their excellent oxygen barrier properties. Using distinct layers of differing materials is not preferred, however, because it adds cost to packaging construction and does not reduce the levels of oxygen already present in the package matrix.

Alternatively, adding oxygen scavenging agents to the PET resin is known as active-barrier packaging. This approach to protecting oxygen-sensitive products is two-fold; the packaging prevents oxygen from reaching the product from the outside, and also absorbs some of the oxygen present in the article and from within the polymer matrix. In some applications, small packets or sachets containing oxygen scavenging agents are added to the packaging article and lie next to the food. Sachets are generally limited to solid foods, where the sachet can be readily removed from the foodstuff and not accidentally ingested. The construction of the sachets and the cumbersome nature of their introduction into packages also result in increased costs.

One way to overcome the disadvantages of sachets is to incorporate the oxygen scavenging agent directly into the packaging article. This can be done by dispersing the scavenging composition throughout the packaging article or by placing the scavenging composition in a unique layer between many layers of the packaging article. At present, the incorporation of an oxygen scavenging agent throughout the packaging article can be found in non-transparent trays and packaging films where the oxygen scavenging agent is not visible and does not become visible to the users of the trays or films. Virtually any oxygen scavenging agent can be used in those applications because the scavenger is not visible in the opaque trays or films. However, packaging articles such as containers, bottles, clear wraps, trays, and the like, requiring higher clarity have heretofore been limited to organic type oxidizable compositions that maintain their clarity when used as a separate layer of the packaging article. Unfortunately, the use of organic type oxygen scavenging agents in a mono-layer or single-layer construction is limited by cost, off-flavors, and regulatory constraints due to the nature of the

organic scavenger or the by-products of the scavenging (*i.e.*, reduction/oxidation) reaction.

Further contributing to the cost are the logistical problems encountered with the use of organic type scavengers. In most embodiments, a transition metal catalyst is used to activate the organic oxidizable composition. A disadvantage of this technique is that the organic composition begins reacting with oxygen as soon as the package is made. Consequently, where packaging articles such as containers or bottles must be filled, they must be filled immediately. Additionally, higher amounts of organic oxygen scavenging agents are used to compensate for the scavenging capacity lost between the time the bottle is made and the time the bottle is filled.

In another technique, UV radiation is used to activate the organic oxidizable composition. However, UV activation techniques are relatively expensive, and the initiators are often not regulated for use in food packaging. Packages designed for beers and juices are specifically designed to prevent UV penetration; hence UV activation would not be practical for those containers which block UV.

An alternative to a visually acceptable organic material is to use discrete, inorganic oxygen scavenging particles in the packaging article, such as reduced metal powders. Reduced iron powder is commonly used for oxygen scavenging in many food packages. Iron reacts with the oxygen and forms iron oxide. Most applications also utilize a salt and/or a moisture absorber as reaction-enhancing agents to increase the effectiveness of the iron powder. Advantageously, because the reaction usually requires water, the iron scavenging composition remains inactive until the wall or wrap of the package contacts the product. Water from the packaged product migrates into the polymer matrix and contacts the scavenging composition, thus activating the reaction.

Unfortunately, the use of scavenging iron powders in packages requiring high clarity has heretofore been limited by aesthetics and the cosmetic appearance of the packages, particularly haze and color. High loadings of iron powder, on the order of 500 - 5000 parts per million, are typically required to obtain sufficient

oxygen absorption. Previous efforts have focused on how to overcome the haze and color effects of scavengers in unfilled containers. However, additional aesthetic problems are encountered after the container is filled and stored for a period of time, during which the inorganic scavenging agent reacts with oxygen, *i.e.* is oxidized, within the polymer matrix. For example, the reaction of the inorganic scavenging powder particles with oxygen may increase the particle size and even change the particle's color. After oxidation has occurred, particles that are initially invisible to the naked, unaided eye become visible dots or spots. Visibility typically occurs within a period of hours or days, depending upon the type, amount and size of the oxygen scavenging agent and capacity to scavenge oxygen. These visual defects, *i.e.*, the visible spots, are aesthetically undesirable and essentially ruin the cosmetic appearance and consumer acceptance of the article.

Thus, there remains a need for less costly, transparent packaging articles, such as films, containers and bottles, comprising inorganic oxygen scavenging agents that maintain acceptable visual aspects, *i.e.*, are devoid of visible spots, for significant period of time after filling the article or coming into contact with the product being packaged.

BRIEF SUMMARY OF THE INVENTION

Broadly, the present invention is directed towards the production of a transparent article, such as a plastic film, container or bottle, including a thermoplastic polymer matrix and an effective amount of an inorganic oxidizable composition, also identified herein as an oxygen scavenger composition, wherein the article does not have domains that are created upon formation of the article visibly appearing in the article after initiation of an oxidation reaction for a commercially sufficient amount of time, typically on the order of at least about 3 months or more, and without resorting to special environmental conditions. As noted hereinabove, such articles comprising a thermoplastic polymer matrix and an inorganic oxidizable composition, particularly when stretched, will typically produce visible spots within the polymer matrix of the article shortly, *i.e.*, within 3

months, after the oxidation reaction is initiated. The initiation of the oxidation reaction typically occurs after the article is filled or otherwise comes into contact with a product that contributes water. These spots are produced by the oxidation of the inorganic composition, at least initially within domains created in the polymer matrix upon formation of the article and containing the inorganic oxidizable composition.

It has been unexpectedly found that by reducing significantly the size, and more particularly, the shortest dimension of the domains created during formation of the article, the spots do not become visible to the naked eye. That is to say, while the spots are effectively still being created upon oxidation of the oxygen scavenging agent, the spots are invisible because the projected area or volume of the domains where the oxidation reaction occurs is so small that the oxidized domains cannot be seen by the naked eye. Thus, it has been found that by controlling the size dimensions of the domains created in the article, particularly in the dimensions in the axial plane of the article, one can effectively control the size of the spots created upon the reaction of oxygen with the oxidizable composition. In particular, it has been discovered that where the shortest dimension of each domain created upon formation of the article, as measured in the axial plane of the article, is maintained at up to about 45 microns, no visible spots will occur in the article unless or until the oxidized components break out of the domain (which it may do very slowly over a much longer period of time) and the shortest dimension becomes greater than 45 microns.

The advantages of the present invention over the existing prior art relating to transparent articles employing oxygen scavengers, which shall become apparent from the description and drawings that follow, are accomplished by the invention as hereinafter described and claimed.

In general, the present invention provides a thermoplastic polymer matrix and a plurality of domains, dispersed in the thermoplastic polymer matrix and having dimensions in an axial plane of the article, each domain encompassing an oxidizable inorganic composition, wherein the shortest dimension of each domain in the axial plane of the article is up to about 45 microns, so as to

substantially preclude visibility of the domains to a naked eye resulting from oxidation of the inorganic composition within the domain as well as oxidation of the inorganic composition that exceeds the domain but does not exceed up to about 45 microns.

5 One or more other aspects of the present invention are provided by a method for the production of a transparent article including a thermoplastic polymer matrix having an inorganic oxidizable composition dispersed therein, comprising adding an effective amount of the inorganic oxidizable composition into the polymer matrix to scavenge oxygen passing through the polymer matrix; forming
10 an article of desired size and shape, wherein domains are created around the inorganic oxidizable composition upon formation of the article, the domains having dimensions in the axial plane of the article, and wherein the shortest dimension of each domain is up to about 45 microns, so as to substantially preclude visibility of the domains to the naked eye resulting from oxidation of the inorganic composition
15 within the domain as well as oxidation of the inorganic composition that exceeds the domain but does not exceed up to about 45 microns.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a representative sectional, perspective view of a part of an
20 article illustrating domains containing an inorganic oxidizable composition dispersed within a thermoplastic polymer matrix;

Fig. 2 is a representative cross-sectional view of a shaped, stretched article also illustrating domains containing an inorganic oxidizable composition dispersed within a thermoplastic polymer matrix;

25 Fig. 3 is an enlarged sectional view of one domain with the thermoplastic matrix of the article of Fig. 2; and

Fig. 4 is a an enlarged sectional view of the domain of Fig. 3 taken along the line 4-4 in Fig. 3.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, shaped transparent articles, comprising a thermoplastic polymer matrix having an inorganic oxidizable composition dispersed therein, are provided, wherein domains in the article, normally visible to the naked eye of the ordinary observer upon oxidation of the inorganic composition upon contacting the article with a product which contributes water, such as by filling a container with a liquid, have been substantially precluded from readily becoming a size visible to the naked eye of the ordinary observer. Thus, domains, even when filled with oxidized material, will not form visible spots. Such articles are especially useful in the packaging industry when in the form of a container or bottle.

As noted hereinabove, the present invention solves the "visual spots" problem present in transparent articles by controlling the dimensions of the domains created in the polymer matrix upon formation of the article. According to the present invention, by maintaining the size of the domains such that the shortest dimension in the axial plane of the article is less than 45 microns, the visibility of the spots will be substantially precluded. By the term "substantially precluded," it is first meant that essentially no spots will be visible in the article after initiation of an oxidation reaction in the domain for a period of time as to permit the delivery and storage of product contained by or contacting the article in practical commercial use, such use including a shelf life of at least about 3 months. It is also meant that, to the extent that any spots are found in the article, there are so few as to be *de minimus* and not of concern with respect to the commercial acceptability of the article. Generally, commercial acceptance will not allow more than 2 spots per square centimeter of the article.

In addition, it will be appreciated, as noted above, that the present invention does not prevent oxidation of the inorganic composition, and thus, does not prevent the production of spots. The invention does, however, prevent the production of visible spots over a significantly longer period of time than has been previously realized by other efforts in the art. Eventually, the inorganic composition will oxidize so much that it will not be contained by the domains

created in the polymer matrix, and will break through the natural barrier of the domains and into the polymer matrix. Once it does, the oxidized composition will continue to grow. Once the shortest dimension of the oxidized composition exceeds 45 microns, the "spot" will become visible to the naked eye.

5 To be "visible to the naked eye", the oxidized domains or spots must be visible to the ordinary observer when a non-labeled, non-colored, non-opaque article is positioned 2 feet away from him in indirect room light, which is about 650 lumens. In the present invention, the oxidized domain or spot should remain invisible for at least 3 months of aging.

10 Aging commences upon contacting the article with water or other substance, typically a liquid, which consumes oxygen, and continues for as long as the substance remains in contact with the article. In most instances, the article will be a container or bottle such that the container can simply be filled with the water or other liquid. While the following description refers to a liquid or other
15 substance filling a container, it will be understood that contacting an article in other ways may also fall within the scope of the present invention.

 A test for determining the container's ability to substantially preclude visible spots, or to otherwise "age" the container, can be accomplished by filling the container with an oxygen-consuming liquid. To be an oxygen-consuming liquid,
20 the liquid must have a pH lower than 7.0 and have ingredients that rapidly consume oxygen. Examples are liquids with dissolved citric acid, vitamin E, or sulfites. It is important to have the oxygen consuming material in the liquid. Otherwise, any oxygen that passes through the container wall will dissolve into the liquid and remain available to react with the scavenger. Analysis without the
25 oxygen reactant in the liquid overstates the amount of actual reaction and will lead to a shorter time for the bloom, *i.e.*, the oxidation of the inorganic composition resulting in spots in the container, to occur. This also eliminates distorted results from non-barrier caps that would allow more oxygen to ingress than would ingress during commercial conditions.

30 After filling the container brimful, the container is capped and stored at ambient conditions, typically 23°C and 50% relative humidity. It is critical to make

sure that residual, oxygen-reactive materials remains in the liquid throughout the testing cycle. This insures that the test integrity is maintained during the complete storage time. Any standard test for citric Acid, vitamin C, or the reactive sulfite form is suitable. Quantification of the reactive ingredient is not essential.

5 Referring now to the drawings, a section of a shaped, transparent article, generally indicated by the numeral 10 in Fig. 1, is illustrated. As shown, the section 10 has been stretched in all directions within the axial plane of the article, including both the radial (X) and axial (Y) directions, as indicated by the arrows. By the term "axial plane," it is meant that the general plane of the article is
10 essentially parallel to the surface of the article, or put another way, that the general plane of the article is substantially perpendicular to the line of sight of the observer.

The section 10 comprises a thermoplastic polymer matrix 12 having discrete oxygen scavenging particles 14 of an inorganic oxidizable composition
15 dispersed therein. Given that the inorganic oxidizable composition is not extensible or deformable and assuming that the thermoplastic polymer matrix 12 is, it will be appreciated that voids 16 will be created around the discrete particles 14 in the polymer matrix 12 upon stretching of the article. Assuming the use of spherical inorganic oxygen scavenging particles 14 upon blending in the polymer
20 matrix 12, and where the particles 14 have been dispersed uniformly and an article has been stretched evenly in all directions within the axial plane, a cross-section of the voids 16 would be, in theory, circular, as shown here and in Fig. 4, when viewed perpendicular to the axial plane. In practice however, dispersion of the particles 14 and stretching of the article are not uniform and irregular-shaped voids
25 16 are most often created, having various length, width and height dimensions.

It will be understood that the polymer matrix need not be extremely extensible and deformable for the present invention, it being understood that where significant stretching does not occur, a smaller void will occur. That is, the more the polymer matrix is stretched, the larger the void 16 surrounding the
30 inorganic particle in the polymer matrix will become upon formation of the article by certain techniques such as blow molding and the like. If no stretching occurs,

there is likely no void at all. Essentially any formation technique may also be adopted for the production of the article. It is recognized that some of these techniques may not stretch the polymer matrix away from the inorganic oxidizable composition very much, if at all. That is, the circumference of the void 16 may be
5 nearly the size of the particle 14. Or, in the special case where the domain is the same size as the particle, there is no void. Nevertheless, for purposes of understanding this invention, the drawings employ an extensible, deformable polymer matrix 12. It is also known that, oftentimes, given the irregular shapes that may form, two or more of these discrete particles 14 of the inorganic
10 oxidizable composition may come together to form one larger structure.

Unlike the representative drawing, sectioning the article along any one specific axial plane will penetrate the voids 16 at various places through the height of each void unless, as shown here, all voids 16 and particles 14 are evenly parallel on the specific axial plane. Thus, some discrete particles and their surrounding
15 voids should appear smaller than others on any one specific axial plane. Likewise, cutting the article along any one specific transverse plane will penetrate the discrete particles and surrounding voids at various places through the length and/or width of each discrete void unless the particles and voids are unidirectionally stacked on each other within that plane. Thus, some discrete
20 particles and voids should appear longer than others on any one specific axial plane.

In Fig. 2, a section of a wall of a shaped article, generally indicated by the numeral 20, is illustrated. Such an article may be a plastic container or bottle. As described previously for Fig. 1 above, this section 20 of the article includes a
25 thermoplastic polymer matrix 22 having discrete oxygen scavenging particles 24 of an inorganic oxidizable composition dispersed therein and surrounded by voids 26. Based upon the Fig. 3 and 4, it will be appreciated that this article 20 is also oriented or stretched in all directions within the axial plane of the article, in a manner similar to that shown in Fig. 1.

30 Figs. 3 and 4 are sectional views illustrating enlargement of a section of the shaped article of Fig. 2, wherein the oxygen scavenging particle 24 is contained

in the void 26 and is entrapped within the polymer matrix 22. Again, where the polymer matrix is not an extensible, deformable thermoplastic polymer, the entire area or volume denoted by the numeral 26 will be shrunk to nearly match that of the of discrete oxygen scavenging particle 24. Again, however, for the purposes of clarity of the present invention, the drawings show an extensible polymer matrix, such as a polyester matrix, wherein the voids 26 would result from the shaped article being stretched as discussed hereinabove.

Notable, as shown in the drawings, upon formation of the article, a domain 28 is created in the polymer matrix 22 that essentially includes both the discrete oxygen scavenging particle 24 and void 26 surrounding the particle. Where less deformable, substantially inextensible polymers are utilized as the thermoplastic polymer matrix, the void 26 formed will generally be *de minimus* and nearly match the size of the particle 24. However, as a preferred embodiment of the present invention, deformable and extensible polymer matrices and non-deformable oxygen scavenging particles are utilized, and therefore, a domain 28 includes not only the volume of the oxygen scavenging particle 24, but also the additional volume in the article of the void 26 between the oxygen scavenging particle 24 and the polymer matrix 22. Furthermore, where the article has not been stretched, the domain will essentially match the volume of the oxygen scavenging particle.

The present invention is particularly concerned with those domains created upon formation of the article having dimensions in the axial plane of the article. In particular, the present invention requires the shortest dimension of each domain in this axial plane to be less than 45 microns, more preferably, less than 38 microns, and even more preferably, less than 32 microns.

The length dimension of a domain is the diameter of the domain as measured across the widest or longest portion of a domain split equally in half within a particular plane, here the axial plane. The width dimension in the axial plane is that diameter of the domain as measured across the widest portion of the domain perpendicular to the length dimension in that plane. As the length dimension will always be the "longest dimension" in the axial plane, the width

dimension will be the “shortest dimension” in the axial plane as defined for purposes of the present invention. In other words, the “shortest dimension” is the minor axis of the ellipse circumscribed by the edges of the domain in the axial plane. Thus, in Fig. 3, the dimension seen as extending from one end 29 to the other end 29' of the domain may be either the width or the length dimension of the domain, depending upon the measurement of the dimension perpendicular to that dimension in that axial plane, *i.e.*, the dimension of the domain as going into the paper.

In Fig. 4, the dimension of the domain shown is any diameter of the circle. That diameter will be not only the longest dimension, but also the shortest dimension in the axial plane. However, it will be appreciated that more often the domain in the axial plane of the article will be ellipsoidal in nature and will have a longer diameter in one direction, say the Y direction, than in another, say the X direction. In this instance, the longest dimension in the axial plane would be the longest diameter of the domain (in this scenario, in the axial (Y) direction), while the shortest dimension in the axial plane would be the longest or widest diameter in the other, perpendicular direction (here, in the radial (X) direction). It has been found that, upon oxidation of the inorganic oxidizable composition in the domains, domains having a shortest dimension in the axial plane as defined hereinabove of less than 45 microns will not show up in the article as visual spots. Thus, the maintaining control of at least the size of the shortest dimension of the domains created in the polymer matrix upon formation of the article will enable the manufacturer of the articles to produce transparent articles devoid of spots.

Articles of the present invention are not necessarily limited to stretching in all directions, (known as “biaxial orientation”), but may be stretched unidirectionally as well. Indeed, the article may not be stretched at all. In the unidirectional process of stretching, articles are stretched in only the radial (X) or axial (Y) direction. It will be appreciated that using this different process technique, not only does the size and shape of the article change, but also the size and shape of the domain changes. More specifically, the void formed around the oxygen scavenging particle due to stretching will be significantly different, and

therefore, the dimensions of the domains in the axial plane will be different. In the situation of unidirectional stretching, it will be appreciated that the shortest dimension in the axial plane will essentially be the diameter of the inorganic oxidizable composition.

5 Turning to the components of the article, the present invention includes a thermoplastic polymer matrix having an inorganic oxidizable composition dispersed therein. The major component of the article of the present invention is the thermoplastic polymer matrix. Suitable thermoplastic polymers for use in the present invention include any thermoplastic homopolymer, copolymer, or
10 terpolymer, or blends thereof. Examples of thermoplastic polymers include polyamides, such as nylon 6, nylon 66 and nylon 612, nylon MXD6, linear polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate, and polyethylene naphthalate, branched polyesters, polystyrenes, polycarbonate, polyvinyl chloride, polyvinylidene
15 dichloride, polyacrylamide, polyacrylonitrile, polyvinyl acetate, polyacrylic acid, polyvinyl methyl ether, ethylene vinyl acetate copolymer, ethylene methyl acrylate copolymer, polyethylene, polypropylene, ethylene-propylene copolymers, poly(1-hexene), poly(4-methyl-1-pentene), poly(1-butene), poly(3-methyl-1-butene), poly(3-phenyl-1-propene) and poly(vinylcyclohexane). Preferably, the
20 thermoplastic polymer used in the present invention comprises a polyester polymer or copolymer, or a blend of a polyester and a polyamide.

It will be understood that the thermoplastic polymer suitable for use in the present invention can be made into a film, sheet, or injection molded article. The present invention is not, however, limited to films and sheets. The article of
25 the present invention also includes containers, bottles, trays, bases, lids, etc. Such article may be manufactured or formed into a desired size and shape using any processing techniques known in the art, including blow molding, injection molding, extrusion, and the like.

Polymers employed in the present invention can be prepared by
30 conventional polymerization procedures well known in the art. The polyester polymers and copolymers may be prepared by melt phase polymerization involving

the reaction of a diol with a dicarboxylic acid, or its corresponding diester. Various copolymers resulting from use of multiple diols and diacids may also be used. Polymers containing repeating units of only one chemical composition are homopolymers. Polymers with two or more chemically different repeat units in the same macromolecule are termed copolymers. The diversity of the repeat units depends on the number of different types of monomers present in the initial polymerization reaction. In the case of polyesters, copolymers include reacting one or more diols with a diacid or multiple diacids, and are sometimes referred to as terpolymers.

Suitable dicarboxylic acids include those comprising from about 6 to about 40 carbon atoms. Specific dicarboxylic acids include, but are not limited to, terephthalic acid, isophthalic acid, naphthalene 2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, 1,3-phenylenedioxydiacetic acid, 1,2-phenylenedioxydiacetic acid, 1,4-phenylenedioxydiacetic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like. Specific esters include, but are not limited to, phthalic esters and naphthalic diesters.

These acids or esters may be reacted with an aliphatic diol having from about 2 to about 10 carbon atoms, a cycloaliphatic diol having from about 7 to about 14 carbon atoms, an aromatic diol having from about 6 to about 15 carbon atoms, or a glycol ether having from 4 to 10 carbon atoms. Suitable diols include, but are not limited to, 1,4-butanediol, trimethylene glycol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, diethylene glycol, resorcinol, and hydroquinone.

Polyfunctional comonomers can also be used, typically in amounts of from about 0.1 to about 3 mole percent. Suitable comonomers include, but are not limited to, trimellitic anhydride, trimethylopropane, pyromellitic dianhydride (PMDA), and pentaerythritol. Polyester-forming polyacids or polyols can also be used.

One preferred polyester is polyethylene terephthalate (PET) formed from the approximate 1:1 stoichiometric reaction of terephthalic acid, or its ester, with ethylene glycol. Another preferred polyester is polyethylene naphthalate (PEN)

formed from the approximate 1:1 to 1:1.6 stoichiometric reaction of naphthalene dicarboxylic acid, or its ester, with ethylene glycol. Yet another preferred polyester is polybutylene terephthalate (PBT). Copolymers of PET, copolymers of PEN, and copolymers of PBT are also preferred. Specific co- and terpolymers of interest are
5 PET with combinations of isophthalic acid or its diester, 2,6 naphthalic acid or its diester, and/or cyclohexane dimethanol.

Polyester has excellent optical properties, even when crystallized through strain hardening (stretching). The oxygen-scavenging particles of the present invention are incompatible with polyester resin. In other words, the
10 particles do not dissolve in the resin, but remain as discrete particles. During orientation and stretching, these discrete particles initiate the formation of voids around or adjacent to the particles. The number of particles and the size of the particles affect the number and size of the voids in stretched films and articles. Additionally, the degree and direction of stretching affect the size and shape of the
15 voids. Accordingly, the size of the oxygen-scavenging particles can vary widely.

The esterification or polycondensation reaction of the carboxylic acid or ester with glycol typically takes place in the presence of a catalyst. Suitable catalysts include, but are not limited to, antimony oxide, antimony triacetate, antimony ethylene glycolate, organomagnesium, tin oxide, titanium alkoxides,
20 dibutyl tin dilaurate, and germanium oxide. These catalysts may be used in combination with zinc, manganese, or magnesium acetates or benzoates. Catalysts comprising antimony are preferred.

Another preferred polyester is polytrimethylene terephthalate (PTT). It can be prepared by, for example, reacting 1,3-propanediol with at least one
25 aromatic diacid or alkyl ester thereof. Preferred diacids and alkyl esters include terephthalic acid (TPA) or dimethyl terephthalate (DMT). Accordingly, the PTT preferably comprises at least about 80 mole percent of either TPA or DMT. Other diols which may be copolymerized in such a polyester include, for example, ethylene glycol, diethylene glycol, 1,4-cyclohexane dimethanol, and 1,4-
30 butanediol. Aromatic and aliphatic acids which may be used simultaneously to make a copolymer include, for example, isophthalic acid and sebacic acid.

Preferred catalysts for preparing PTT include titanium and zirconium compounds. Suitable catalytic titanium compounds include, but are not limited to, titanium alkylates and their derivatives, titanium complex salts, titanium complexes with hydroxycarboxylic acids, titanium dioxide-silicon dioxide-co-precipitates, and
5 hydrated alkaline-containing titanium dioxide. Specific examples include tetra-(2-ethylhexyl)-titanate, tetrastearyl titanate, diisopropoxy-bis(acetyl-acetonato)-titanium, di-n-butoxy-bis(triethanolaminate)-titanium, tributylmonoacetyltitanate, triisopropyl monoacetyltitanate, tetrabenzoic acid titanate, alkali titanium oxalates and malonates, potassium hexafluorotitanate, and titanium complexes with tartaric
10 acid, citric acid or lactic acid. Preferred catalytic titanium compounds are titanium tetrabutylate and titanium tetraisopropylate. The corresponding zirconium compounds may also be used.

The polymer of this invention may also contain small amounts of phosphorous compounds, such as phosphates, and a catalyst such as a cobalt
15 compound, that tends to impart a blue hue.

The melt phase polymerization described above may be followed by a crystallization step, then a solid phase polymerization (SSP) step to achieve the intrinsic viscosity necessary for bottle manufacture. The crystallization and polymerization can be performed in a tumbler dryer reaction in a batch-type
20 system. Alternatively, the crystallization and polymerization can be accomplished in a continuous solid state process whereby the polymer flows from one vessel to another after its predetermined treatment in each vessel.

The crystallization conditions preferably include a temperature of from about 100°C to about 150°C. The solid phase polymerization conditions
25 preferably include a temperature of from about 200°C to about 232°C, and more preferably from about 215°C to about 232°C. The solid phase polymerization may be carried out for a time sufficient to raise the intrinsic viscosity to the desired level, which will depend upon the application. For a typical bottle application, the preferred intrinsic viscosity is from about 0.65 to about 1.0 deciliter/gram, as
30 determined by ASTM D-4603-86 at 30 °C in a 60/40 by weight mixture of phenol

and tetrachloroethane. The time required to reach this viscosity may range from about 8 to about 21 hours.

In one embodiment of the invention, the thermoplastic polymer matrix of the present invention may comprise recycled polyester or materials derived from recycled polyester, such as polyester monomers, catalysts, and oligomers.

The other component of the article is an inorganic oxidizable composition dispersed in the polymer matrix. An inorganic oxidizable composition is an oxygen scavenging agent, and the two can be used interchangeably. The inorganic composition preferably includes an oxidizable metal. The metal may be employed in an effective amount to scavenge oxygen at least as it passes through the polymer matrix of the article. These oxygen scavenging metals may be selected from the group consisting of calcium, magnesium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, silver, tin, aluminum, antimony, germanium, silicon, lead, cadmium, rhodium, and combinations thereof. More preferably, the oxygen-scavenging particles comprise an oxygen scavenging metal selected from calcium, magnesium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, or tin. Even more preferably, the oxygen scavenging metal is iron.

It will be understood that these oxygen scavenging metals may be present as mixtures, in compounds such as oxides and salts, or otherwise combined with other metals, with the proviso that the oxygen-scavenging metals are capable of reacting with molecular oxygen. Metal alloys comprising at least one oxygen-scavenging metal are also suitable. The oxygen scavenging metals may contain impurities that do not affect the nature or practice of the present invention.

Desirably, agents are selected that do not react with oxygen so quickly that handling of the materials is impracticable. Therefore, stable oxygen scavenging agents that do not readily explode or burn upon contact with molecular oxygen are preferred.

It is known in the art that certain substances enhance the oxygen scavenging reaction. Therefore, the oxygen scavenging agents may optionally comprise one or more reaction enhancing agents. The reaction enhancing agents,

like the oxygen scavenging metals, are typically present in the form of discrete particles. In a preferred embodiment of the present invention, the oxygen scavenging metals are pre-treated with one or more reaction-enhancing agents that facilitate the oxygen scavenging reaction. Any of the reaction-enhancing agents known in the art may be used. Examples of known reaction-enhancing agents are discussed in U.S. Pat. Nos. 5,744,056 and 5,885,481, hereby incorporated by reference in their entirety. Suitable agents are variously described as hygroscopic materials, electrolytic acidifying agents, non-electrolytic acidifying agents, metal halides, metal sulfates, metal bisulfates, and salts. The reaction-enhancing agents may be added to the polymer melt, or during extrusion.

In one embodiment of the present invention, the oxygen scavenging agent comprises iron. The iron reacts with oxygen in its function as an oxygen scavenger. Metallic iron, or alloys or mixtures containing metallic iron may be used. Furthermore, it is to be understood that the metallic iron may contain impurities that do not affect the practice of the present invention.

At least four types of metallic iron powders are available: electrolytic, sponge, carbonyl, and nanoparticle iron made by a number of different processes. Electrolytic iron is made via the electrolysis of iron oxide, and is available in annealed and unannealed form from, for example, North American Höganäs, Inc. Sponge iron is also available from, for example, North American Höganäs, Inc. There are at least two types of sponge iron: hydrogen-reduced sponge iron carbon monoxide-reduced sponge iron. Carbonyl iron powder is available from, for example, Reade Advanced Materials. It is manufactured using a carbonyl decomposition process. Nanoparticles iron is a fairly recent advance in the art and may or may not be currently available at commercially viable economics.

Depending upon the type of iron selected, the particles may vary widely in purity, surface area, and particle shape. The following non-limiting examples of typical characteristics are included herein to exemplify the variation that may be encountered. Electrolytic iron is known for its high purity and high surface area. The particles are dendritic. Carbonyl iron particles are substantially uniform spheres, and may have a purity of up to about 99.5 percent. Carbon monoxide-

reduced sponge iron typically has a surface area of about 95 square meters per kilogram (m^2/kg), while hydrogen-reduced sponge iron typically has a surface area of about 200 m^2/kg . Sponge iron may contain small amounts of other elements, for example, carbon, sulfur, phosphorus, silicon, magnesium, aluminum, titanium, 5 vanadium, manganese, calcium, zinc, nickel, cobalt, chromium, and copper.

The oxygen scavenging agents are present in an effective amount for adequate oxygen scavenging ability. If too few oxygen scavenging particles are present, too much oxygen may be able to pass through the article without being scavenged. The amount required for adequate oxygen scavenging ability depends 10 on such factors as the application, the type of polymer used, the amount of gas barrier protection desired, the type of oxygen scavenging particles, the particle size of the oxygen scavenging particles, and moisture content of the packaged material. Preferably, the article of the present invention comprises at least about 50 parts oxygen-scavenging particles per million parts by weight resin. More preferably, the 15 article of the present invention comprises at least about 100 parts oxygen-scavenging particles per million parts by weight resin. Even more preferably, the article of the present invention comprises at least about 500 parts oxygen-scavenging particles per million parts by weight resin. Yet even more preferably, the article of the present invention comprises at least about 1000 parts oxygen- 20 scavenging particles per million parts by weight resin. In the case of nanoparticles iron (particles of a size less than 1 micron), the amount of material may be less than 500 parts oxygen scavenging particles per million parts by weight resin due to its increased surface area.

It has been found that transparent articles, such as films or bottles, 25 comprising up to about 12,000 parts oxygen-scavenging particles per million parts by weight resin (1.2 weight percent) can have minimal visual defects, *i.e.*, no spots, as well as acceptable haze and color characteristics. For applications where these optical characteristics are not an issue of concern, it will be appreciated that the amount of oxygen scavenging or other particles may be much higher. Further 30 characterization of the particles of the present invention that may be useful for practice of the present invention is provided hereinbelow.

In scavenging the oxygen, the article provides a longer shelf life for oxygen-sensitive materials that may be packaged therein. Preferably, the size of the scavenging domain is optimized to impart effective scavenging activity to the article, while minimizing the number of visual defects or spots in the article after
5 scavenging of the oxygen, i.e., oxidation of the inorganic composition, has occurred. From a standpoint of food safety, materials of low toxicity are preferred, however with proper precautions, this is not a limitation. The particles should not adversely affect the organoleptic properties of the final product.

The composition of the present invention may optionally yet further
10 comprise one or more components selected from the group consisting of impact modifiers, surface lubricants, denesting agents, stabilizers, crystallization aids, antioxidants, ultraviolet light absorbing agents, catalyst deactivators, colorants, nucleating agents, acetaldehyde reducing agents, reheat reducing agents, fillers, branching agents, blowing agents, accelerants, and the like.

15 It will be understood that if the above-mentioned optional components maintain their discrete nature within the resin, then may contribute to void creation and/or otherwise affect the optical characteristics of the container.

High levels of particles can be incorporated into a polyester resin composition while maintaining minimal visual defects. The particles may be
20 admixed with the thermoplastic polymer during or after polymerization, with the polymer melt or with the molding powder or pellets from which the injection molded articles are formed, or from which the film or sheet is cast. Accordingly, the particles may be added during any of the process steps, such as during melt phase polymerization, after the melt phase polymerization (post polymerization)
25 but before pelletization, during solid state polymerization, and during extrusion. Alternatively, a masterbatch of oxygen-scavenging resin may be prepared, and then mixed or blended with additional resin. Preferably, the masterbatch contains a relatively high amount of particles, and the desired particle concentration in the product polymer is achieved by mixing or blending the masterbatch with an
30 amount of additional resin.

The article of the present invention may advantageously possess both effective oxygen-scavenging functionality and acceptable optical properties. The optical properties of polymers are related to both the degree of crystallinity and the actual polymer structure. Transparency is defined as the state permitting
5 perception of objects through a sample. Transmission is the light transmitted. Transparency is measured as the amount of undeviated light. In other words, transparency is the original intensity of the incident radiation minus all light absorbed, scattered, or lost through any other means.

Many polymers are transparent, but polymers that are transparent to
10 visible light may become opaque as the result of the presence of additives such as fillers, stabilizers, flame retardants, moisture, and gases. The opacity results from light-scattering processes occurring within the material. The light scattering reduces the contrast between light, dark, and other colored parts of objects viewed through the material and produces a milkiness or haze in the transmitted image.
15 Haze is a measure of the amount of light deviating from the direction of transmittancy of the light by at least 2.5 degrees. Generally, the acceptable haziness of an article, such as a bottle or film, is determined visually. However, a HunterLab ColorQuest Spectrometer can quantitatively indicate the haze of an article or resin. This quantitative measurement is referred to herein as transmission
20 Hunter haze.

The color and brightness of a polyester article can be observed visually, and can also be quantitatively determined by a HunterLab ColorQuest Spectrometer. This instrument uses the 1976 CIE a^* , b^* , and L^* designations of color and brightness. An a^* coordinate defines a color axis wherein plus values are
25 toward the red end of the color spectrum and minus values are toward the green end. The b^* coordinate defines a second color axis, wherein plus values are toward the yellow end of the spectrum and minus values are toward the blue end. Higher L^* values indicate enhanced brightness of the material.

Particles larger than about 45 microns in diameter within the polymer
30 matrix are generally visible to the unaided human eye. In a transparent article, these particles appear as discrete visual defects. The color of the particle may also

affect perception of the defect. Particles smaller than about 45 microns in diameter, even if dark in color, are generally not resolvable by the unaided human eye.

5 It will be understood that none of the inorganic particles will be visible in the article unless or until the oxidation reaction is activated. To do this, as discussed hereinabove, the article must be filled or otherwise contact a product being packaged. Upon oxidation, the void in the polymer matrix surrounding the oxidizable composition gets filled with oxidized material. It is this material that is visible to the naked eye as a spot on the article.

10 Oxygen-scavenging particles bloom as they scavenge oxygen. By "bloom" is meant that the particles expand in size, resulting in a larger particle than was originally incorporated into the resin. In addition, depending upon the nature of the oxygen-scavenger, the particle may change color as the scavenging reaction occurs. In a stretched article, the particle may bloom into and partially or
15 even completely fill its associated void. If the rate of oxygen-scavenging is very rapid, or if the reaction is allowed to occur over a long period of time, the bloom may even expand out of the void and into the polymer matrix. In this manner, articles containing oxygen scavenging particles and voids may originally have no visual defects, but may develop visual defects over time, as the oxygen-scavenging
20 particles bloom to a diameter of greater than about 45 microns.

It has now been discovered that no visual domains can be achieved in an oxygen scavenging article, and maintained over a shelf-life of at least about three months and preferably up to about six months, when the shortest dimension of each domain in the axial plane is less than about 45 microns. If the desired shelf-
25 life is less than six months, larger scavenging domains can be tolerated. Moreover, if the rate of oxygen-scavenging is slow, larger scavenging domains can be used. Longer shelf-life and more rapid oxygen-scavenging can be accomplished while maintaining minimal visual defects if the scavenging domains are smaller.

The nature of the oxygen-scavenging particles also affects the amount of
30 bloom and the resultant visual defects. For example, iron is a preferred oxygen-scavenger, and there are substantial differences in the bloom formation among the

different types of iron. More specifically, the bloom associated with a porous sponge iron particle is much smaller than that of a dendritic particle of electrolytic iron of the same original particle size.

5 The article of the present invention may comprise bottles expanded from preforms. A preform is a formed structure that is expanded in a mold to form a bottle. Alternately, the container may comprise film, pouches, or other packaging material.

10 In general, polyester bottles are prepared in blow-molding processes carried out by heating the preform above the polyester glass transition temperature, placing the heated preform into a mold of the desired bottle form, injecting air into the preform to force the preform into the shape of the mold, and ejecting the molded bottle from the mold onto a conveyor belt. Stretching occurs as the preform expands in the mold.

15 It will be understood that, within any particle population, the particles are not all the same size, but comprise a range of particle sizes. Furthermore, the particles within the population may or may not have a uniform, regular shape. The particle population, or any portion of the population, may be described by an average particle size, as measured by any of the standard techniques known in the art. These techniques include measuring the equilibrium velocities of particles
20 settling through a liquid under the influence of gravity, resistance pulse counters, light blockage counters, image analyzers, laser diffraction spectroscopy, and photon correlation spectroscopy. Statistical values commonly used to describe the particle size of a particle population include: (1) geometric mean size, which is the average particle size calculated on a log basis; (2) arithmetic mean, which is the
25 average particle size calculated on a linear basis; (3) median size, which is the 50th percentile of the distribution; and (4) mode size, which is the most prevalent particle size of the distribution. Further, the sample may be described by a particle size range, or as less than or equal to a given particle size. These designations may be determined by sieving techniques, or other techniques known in the art. Thus,
30 any given population of particles will have a particle size distribution, which is a description of the range of particle sizes and the amounts of particles of each size.

Techniques for particle size determination are further discussed by Paul Webb and Clyde Orr in *Analytical Methods in Fine Particle Technology*, Micromeritics Instrument Corp. (1997), and by James P.M. Syvitski in *Principles, Methods, and Applications of Particle Size Analysis*, Cambridge University Press (1991), both of which are hereby incorporated by reference in their entireties.

Various parameters other than the resulting void size have been found to be desirable for the size of particles within the particle population. For example, it will be appreciated that particles larger than the thickness of the container wall may produce a rough surface, so that significant amounts of such large particles are to be avoided. In general, it is preferred that the size of the particles fall within the range of from about 0.001 to about 45 microns, more preferably from about 5 to about 38 microns, and even more preferably from about 10 to about 35 microns. Still even more preferably, the size of the particles may fall within the range of from about 15 to about 32 microns. It will be understood that these preferred ranges are given as general guidelines only, and that a small number of particles may fall outside these ranges without affecting the essential characteristics of the resin, and are therefore within the scope of the present invention.

Likewise, it will be understood that, within the population of scavenging domains, the domains are not all the same size, but comprise a range of domain sizes. Furthermore, the domains within the population may or may not have a uniform, regular shape. The scavenging domain population, or any portion of the population, may be described by microscopic techniques. The average domain size, the average projected surface area, and other features may be determined by microscopic techniques that are known in the art. It will be understood that, where there is no void encompassing or adjacent to a scavenging particle, then the size of that scavenging domain is defined by the size of the particle itself.

For purposes of the present invention, the domain size is measured in the axial plane of the article. The minimum diameter (dimension) is easily envisioned for a circular domain. For an elliptical domain, the minimum diameter is the widest portion of the shortest axis of the ellipse. For a square or rectangular domain, the minimum diameter is the length of the shortest side. For an

irregularly shaped domain, the minimum diameter is the shortest axis of the ellipse approximated by the line encompassing all portions of the domain when viewed in the axial plane.

5 A scavenging domain having a minimum diameter that is greater than about 45 microns is a visual defect. The number of visual defects may be assumed to be the number of scavenging domains having a minimum diameter that is greater than about 45 microns, and may be expressed in terms of number of visual defects per area (*i.e.*, spots/square centimeter) of the article.

10 The article according to the present invention can comprise stretched or unstretched films or sheets of any thickness typically employed in the art of polymer films. In a preferred embodiment, the film may have a thickness of at least about 0.5 mils. Where a container is formed as the article, the container may comprise at least one transparent wall. Preferably, the transparent wall has a transmission Hunter haze number of less than about 10 percent, more preferably
15 less than about 8 percent, and even more preferably less than about 5 percent, per 15 mil wall thickness.

The article of the present invention may be bottles wherein each bottle sidewall has a thickness of from about 9 to about 35 mils, preferably from about 11 to about 25 mils, and more preferably from about 14 to about 21. In a preferred
20 embodiment, each bottle sidewall having a thickness of from about 14 to about 21 mils, has two or fewer visual spots per square centimeter.

In order to demonstrate the practice of the present invention, the following examples have been prepared and tested as described and disclosed hereinbelow. The examples should not, however, be viewed as limiting the scope of
25 the invention. The claims will serve to define the invention.

A 95 mole percent naphthalate/5 mole percent PET copolymer resin was prepared by the teachings of U.S. Pat. No. 5,539,078 , which are incorporated herein by reference. This low molecular weight feed polymer was crystallized and solid state polymerized to prepare a high molecular weight PET base resin.

30 Various types of iron were evaluated at various particle sizes. The electrolytic annealed and un-annealed irons were obtained from OMG Corporation,

now owned by Höganäs. Hydrogen-reduced and carbon monoxide-reduced sponge iron was obtained from Höganäs.

The iron particles were sieved on the following Tyler mesh screens: 325 to 400, 400 to 450, 450 to 500 and 500 to 625. This mesh corresponds to 45 to 38
5 microns, 38 to 32 microns, 32 to 25 microns and 25 to 20 microns, respectively. Each iron type and size was premixed with micronized sodium chloride to create a scavenging composition of 90% iron by weight and 10% weight salt. 4.4 grams of this scavenging composition was mixed with 2000 grams of dried PET resin, resulting in a 2200 parts per million concentration based upon the weight of the
10 composition. This physically blended inorganic oxidizable composition was transferred to a Novotec drying hopper of a Nissei ASB 50T Injection Blow-Molding machine. The hopper was heated to 325°F (163°C) and set for a dew point of - 40 °F (- 40° C), then the bottle preforms were heated and blown into bottles on the Nissei machine.

15 The reactivity of each iron type was determined by removing the same area of the bottle sidewall for each series and placing it into a gas chromatograph vial in the presence of 2 grams of 0.001N acetic acid and de-ionized water respectively. 16 vials were prepared for each series. The oxygen consumption was determined by measuring the O₂ loss in the vial over time. Duplicate oxygen
20 measurements were taken at 0 hours, 24 hours, 48 hours and 72 hours. A plot was made of cc O₂ consumed per gm of PET versus Time. The time to react an equivalent amount of O₂ can be determined.

Once the relative reactivity was determined, the samples were forced to bloom by immersing the sidewall into 20 grams of 0.001N Acetic Acid and storing
25 the vial at 50 °C for the respective time required to react similar amounts O₂.

After reacting with O₂, the sidewall was compared to the unreacted control and examined visually by placing the sidewall against a white background for the presence of identifiable discrete blooms. These were examined microscopically and visually. Those with visual blooms generally had voids with all
30 axes greater than 38 microns.

It should be understood that the void size will vary with the amount of reactivity desired. While the major amount of blooms will show in the first few months, the container will continue to react for a long time with the blooms growing at an ever slower rate. Thus, a bottle which does not have visible blooms
5 at 6 months, may have visible blooms at 12 months. It will be understood that if longer shelf life, and thus, longer reaction times are desired, selection of particles that yield a smaller domain will be required.

An effective amount of scavenging domains is defined as a sufficient number of domains, or amount of scavenging agent, to provide that particular
10 product's required shelf life such that the amount of oxygen reacted over the shelf life of the product does not cause the bloom to grow larger than 38 microns. It is understood that one could put more scavenging agent into the polymer so that each domain reacts less, thereby reducing the size of the bloomed particle.

Thus, it should be evident that the concepts and methods of the present
15 invention are highly effective in providing transparent articles comprising blends of thermoplastic polymers and oxidizable inorganic compositions which do not develop visible spots within the outside, as oxygen passing therethrough is scavenged. The invention is particularly suited for beer beverage bottles, but is not necessarily limited thereto. The concepts and method of the present invention can
20 be used separately with other applications, equipment, methods and the like, as well as for the manufacture of other oriented articles.

Based upon the foregoing disclosure, it should now be apparent that by limiting the size of domains dispersed throughout the polymer matrix to less than 45 microns, the visibility of spots is precluded. Thus, the dispersion of oxidizable
25 inorganic compositions in a plurality of domains, in a continuous polymer matrix in the production of transparent, preferably oriented, articles such as bottles and the like, as described herein, will carry out one or more of the aspects set for the hereinabove. It is, therefore, to be understood that any variations evident fall within the scope of the claimed invention and thus, the selection of specific
30 component elements can be determined without departing from the spirit of the invention herein disclosed and described. In particular, oxidizable inorganic

compositions according to the present invention are not necessarily limited to combinations of iron with sodium bisulfate. Thus, the scope of the invention shall include all modifications and variations that may fall within the scope of the attached claims.